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Short communication

Characteristics of wet and dry crushing methods in the recycling process of spent lithium-ion batteries

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HIGHLIGHTS

- We get the particle size distribution of crushed products of spent LIBs.
- The microscopic morphology and the composition distribution of the <0.25 mm size fractions are analyzed.
- Spent LIBs have good selective crushing property.
- Dry crushing method brings the selective crushing characteristic into full play.

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ABSTRACT

Methods of wet and dry crushing are adopted to experiment on spent lithium-ion batteries in this investigation. Particle size distribution is analyzed using the wet and dry screening respectively and fine crushed products are characterized by XRD, SEM and EDX. A comprehensive comparison of the characteristics between the two crushing methods indicates that the wet crushing results in an enrichment of each component in spent lithium-ion batteries to fine fractions because of the scouring action of water flow, which makes the fine products complicated and lost; while the dry crushing method can bring the selective crushing characteristics of spent lithium-ion batteries into full play, and in this case, lithium cobalt oxide and graphite electrode materials can be liberated from aluminum foil and copper foil without the overcrushing of the other components in spent lithium-ion batteries. Thus, the purity and dispersion of electrode materials can be improved to create favorable conditions for subsequent purification and regeneration.

1. Introduction

In virtue of the advantages such as high energy density, high battery voltage, long charging–discharging cycle, wide temperature range and safe [1,2], the lithium-ion batteries (LIBs) are extensively used in portable electronic equipments. Along with the rapidly increased use of LIBs, the annual global production of LIBs will reach 7 billion in 2015 [3]. After removing the plastic and metal casing, LIBs contain 36 ± 9 wt.% of cobalt and in which high metal content even higher than the processed mineral or ore [4]. However, because of flammable and toxic ingredients in LIBs [5], safe disposal of LIBs has become a tough issue, and thus, the recycling and harmless disposal of spent LIBs has become more and more important.

By now recycling of spent LIBs is still in its infancy. Though there are many recycling methods of spent LIBs, the vast majority of recycling methods are based on hydrometallurgical chemical process and limited to laboratory scale [6–8]. Most recycling research mainly focus on the recycling of $LiCoO_2$ [9–11], while plenty of useful materials are lost during those processes. However, most acquisition of the electrode materials used in the experiments is by manual dismantling method [12–14], and it is obvious that in the recycling process of spent LIBs whose amount are huge and the size are small, manual dismantling is responsible for the low efficiency and high cost. It is, therefore, necessary to develop an effective crushing method for recycling process of spent LIBs.

Mechanical crushing is a key link in the recycling process of E-waste [15]. The combined rate and reaction rate of followed

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chemical, biological methods, separation efficiency and even the choice of subsequent physical methods are directly influenced by the particle size distribution and liberation degree of the crushed products. Though, Shin [10] and Li [16] used crushing methods in their research of recycling process of spent LIBs, until now the research on the crushing properties of spent LIBs has not been reported in detail.

This work aimed at realizing the characteristics of wet and dry crushing methods and mechanical crushing properties of spent LIBs by analyzing the influences of wet and dry crushing methods on the efficient crushing of spent LIBs.

2. Experimental

2.1. Materials and pretreatment

Spent LIBs used in mobile phones of different manufactures and sizes were collected by Environmental Protection Association of China University of Mining & Technology for this study. In order to ensure the safety of the experiment, before crushing, samples were fully discharged for 24 h with 5% mass fraction NaCl solution and then air dried naturally. The total weight of samples was 30 kg, 165.75 g and 133.82 g crushed products of wet and dry crushing respectively were sampled representatively for instrumental analysis.

2.2. Crushing and screening

The wet crushing equipment is a blade crusher with a water medium. Its schematic representation is shown in Fig. 1. Blades are attached to rotating arms in a way that allows the blades to swing freely. As the arms rotate inside the drum the swinging blades contact the feed material at a high speed. This imparts kinetic energy from the blades to the feed, fracturing the feed in the process. High speed feed particles also fracture when they contact other particles or stationary parts of the crusher. Feed that escapes fracture after one impact is hit by the blades again. In this crusher, water is fed into an inlet. This causes the particles to form slurry that carries the broken particles through the sieve plate.

The wet impact crusher was used for wet crushing for 20 s with 500L h^{-1} water consumption. The dry crushing was carried out by a joint two-stage way. Firstly, the spent LIBs were chopped in to pieces by shear crusher and then the products were crushed in the impact crusher for 20 s. Sieve analysis was carried out by Retsch AS-200 automatic screening instrument. Wet and dry screening were used for the Sieve analysis of wet and dry crushed products respectively.

2.3. SEM + EDX analysis

In low vacuum mode, SEM (Quanta 250, FEI, America) and EDX (QUANTAX400-10, Bruke, Germany) were jointly used to analyze the micro-morphology and composition distribution of crushed products.

2.4. XRD analysis

XRD (D8 ADVANCE, Bruke, Germany) was applied to make phase analysis of crushed products. The tube voltage of X-ray was 40 kV and the current was 30 mA. Cu was made as the anode target material. The scanning speed was 0.1 s/step and the interval was 0.019450 (step).

3. Results and discussion

3.1. Sieve analysis

The particle size distribution of crushed products by dry crushing is shown in Fig. 2. Wherein particles larger than 2 mm accounted for 27.57%. While yield of 2–1 mm, 1–0.5 mm, 0.5–0.25 mm three size fractions were only 16.21%, and the particles under 0.25 mm occupied the 56.22% of gross. In comparison, the particle size distribution of crushed products by wet crushing (Fig. 3) described that the yield of fraction larger than 2 mm reached 21.28%. 2–1 mm, 1–0.5 mm, 0.5–0.25 mm three size fractions yielded 30.46%. The total yield of fractions smaller than 0.25 mm in crushed products arrived at 48.26%. Thus it can be seen that the particle size distribution of crushed spent LIBs was not uniform. The coarse size fractions and the fine size fractions were both high while it is low with middle size fractions. That is because LIBs are complex of various materials with different crushing mechanical properties. So, under the same crushing condition, different materials have different particle size distribution. Therefore, the crushing of spent LIBs belongs to selective crushing. However, the performance of selective crushing for dry crushing is obviously better. Given that dry screening is not thorough enough, the actual effect will be better. It means different materials in the dry crushed products can be well separated only by screening.

These results all relate to the structure of spent LIBs: the outermost layer is a plastic shell. The inner core is well encapsulated by aluminum shell with roll type structure which mainly consists of the anode with lithium cobalt oxide pasted on

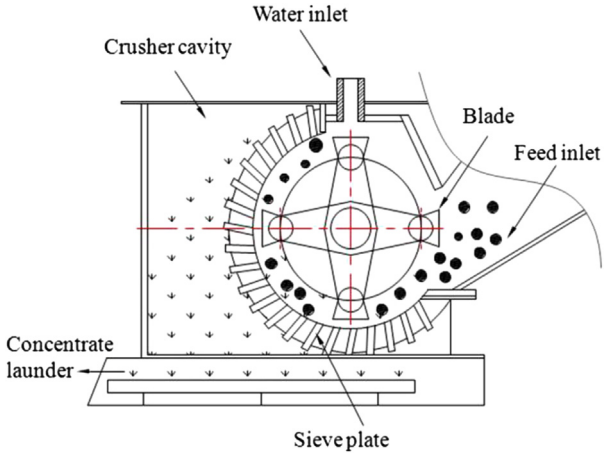

Fig. 1. Sketch of wet impact crusher.

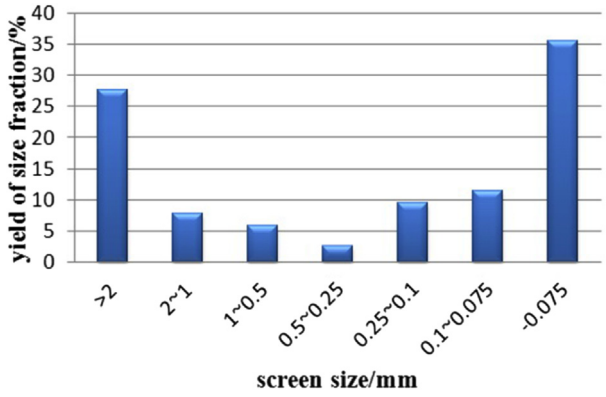

Fig. 2. Particle size distribution of dry crushed products.

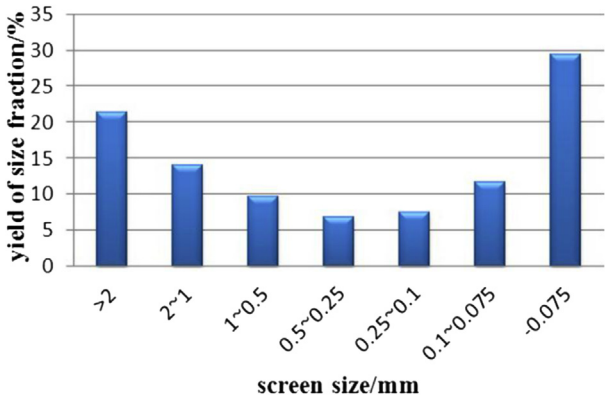

Fig. 3. Particle size distribution of wet crushed products.

aluminum foil, polyethylene membrane, and the cathode with carbon material pasted on copper foil and organic electrolyte. However, active electrode material is fine powder evenly coating on the surface of the copper foil and aluminum foil by binder. Due to the water flow in wet crushing, the crushed products can quickly go through the mesh of the crusher to avoid "over crushing". However, the fine powder can't be liberated from the foils in time, they all pass through the mesh together with water, which lead to an incomplete liberation. In addition, the fine powder of the active electrode materials can easily dissolve into water and that will create further losses.

3.2. Microscopic morphology and element distribution

The distinguished structure of spent LIBs differs from mineral or other solid waste such as discarded printed circuit boards. Internal materials of spent LIBs are mostly separated from each other and wrapped by shells. The crushing of spent LIBs is similar to the "bag breaking" in the municipal waste treatment. Because only electrode materials are not separated which evenly daubed to copper foil and aluminum foil by binder, the liberation of electrode materials from copper foil and aluminum foil is a hot topic in the research of spent LIBs crushing. Besides, the recovery and regeneration of electrode materials of $LiCoO_2$ from spent LIBs is always the research hotspot due to the high price of $LiCoO_2$. In order to study the crushing behavior of these expensive powders clearly, a detailed job was carried out by joint use of SEM and EDX in this investigation.

The partially liberated cathode (lithium cobalt oxide adhered to the aluminum foil) and anode (graphite adhered to the copper foil) of spent LIBs by manual dismantling are shown in Fig. 4, and the amplification is 1500. It can be seen from the figures that the sizes of graphite particles (a) are quite larger than the $LiCoO_2$ particles (b) and $LiCoO_2$ particles have a closer arrangement. In terms of the adhesive agent effect, the indentation generated by the detachment of $LiCoO_2$ in cathode is deeper and that means the adhesion is stronger, and that enlarges the difficulty of the liberation of $LiCoO_2$.

SEM images of each fraction in the crushed products of spent LIBs by wet and dry method are shown in Figs. 5–8. Dry crushed products were screened in a dry way, so fine particles were difficult to be screened well. Therefore, there are finer particles in each fraction under 0.25 mm sizes. But the screen effect of wet crushed

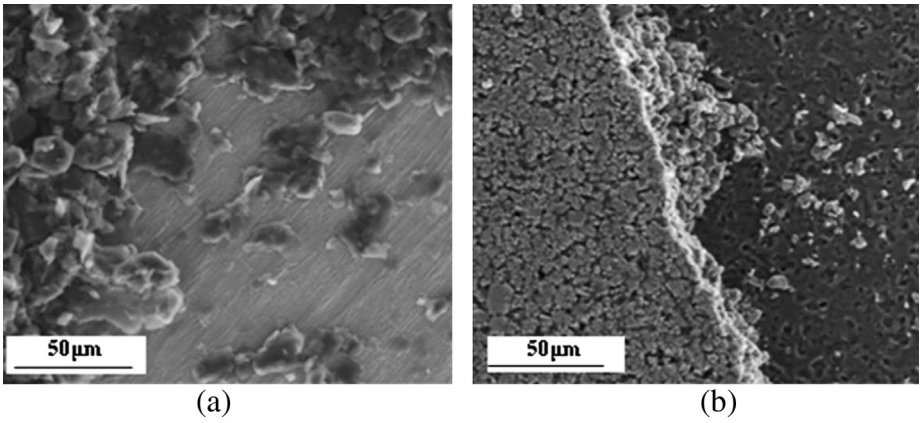

Fig. 4. Electrode materials of spent LIBs: (a) anode electrode, (b) cathode electrode.

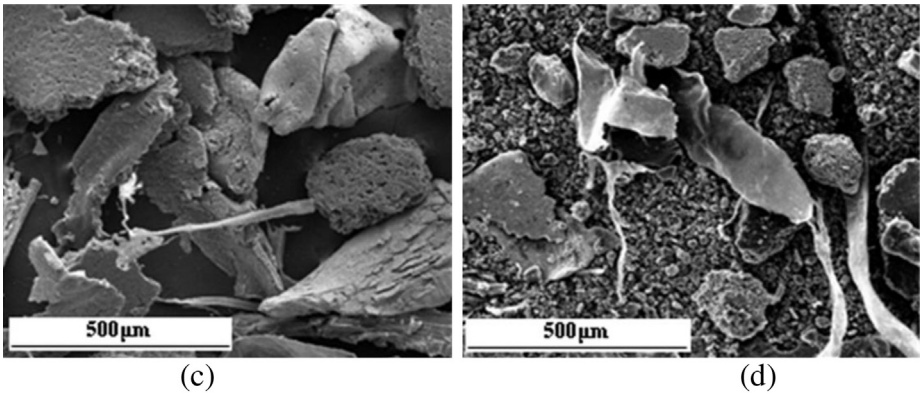

Fig. 5. 0.25–0.1 mm crushed products of spent LIBs: (c) dry crushing, (d) wet crushing.

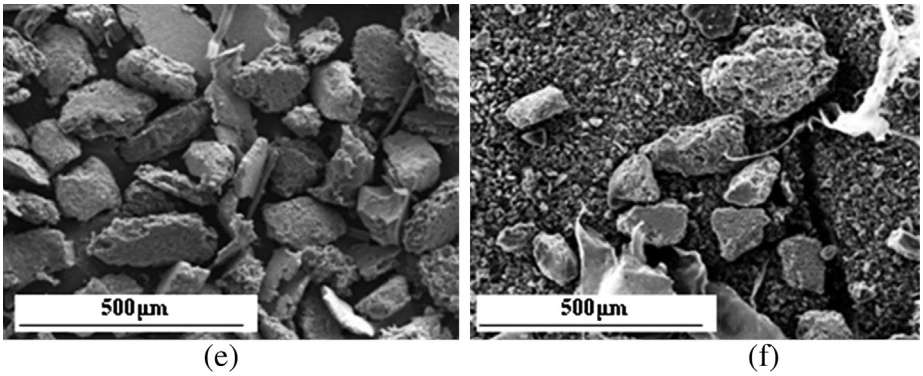

Fig. 6. 0.1–0.075 mm crushed products of spent LIBs: (e) dry crushing, (f) wet crushing.

products with wet screening was better in which particle sizes are homogeneous in each fraction.

Comparing these two kinds of crushed products, it was manifested that under the action of the adhesive, fine particles of active electrode materials ($LiCoO_2$, graphite) in wet crushed products kept the original polymerization condition (it presented as "pancake" after breaking). In 0.25–0.1 mm size fraction, there were graphite, $LiCoO_2$, diaphragm fibers, copper foils, aluminum foils, plastic. Graphite and $LiCoO_2$ with a small amount of diaphragm fibers, copper foils, aluminum foils exist in 0.1–0.075 mm size fraction. −0.075 mm size fraction was mainly composed of loose

Table 1
Element distribution in fine particles of dry crushed products (EDX).

Size fractions	Element (wt.%)							
	O	Al	C	Co	Mn	F	P	Cu
0.25–0.1 mm	13.56	2.18	33.18	46.21	2.02	0.77	1.25	0.84
0.1–0.075 mm	12.69	2.07	32.49	47.58	2.06	0.87	0.84	1.39
<0.075 mm	14.17	2.04	35.05	42.19	2.82	1.47	1.44	0.83

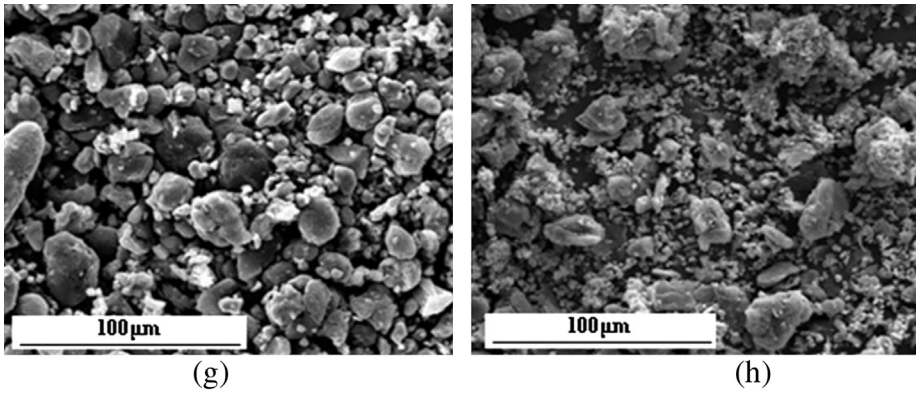

Fig. 7. 0.075–0.045 mm crushed products of spent LIBs: (g) dry crushing, (h) wet crushing.

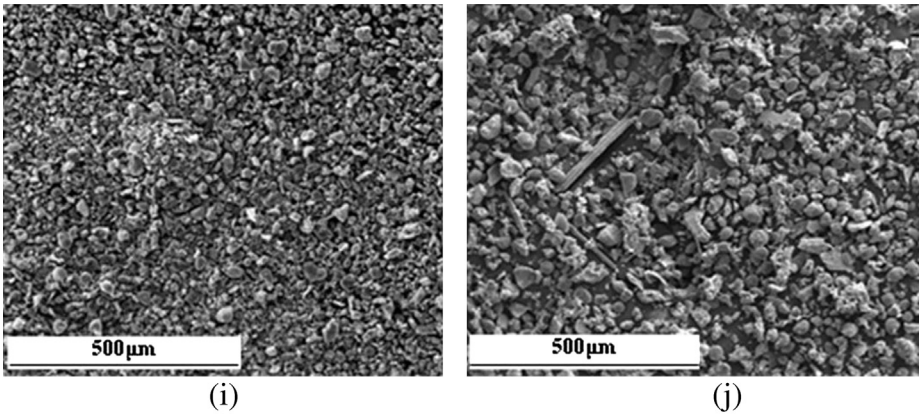

Fig. 8. −0.045 mm crushed products of spent LIBs: (i) dry crushing, (j) wet crushing.

Table 2
Element distribution in fine particles of wet crushed products (EDX).

Size fractions	Element (wt.%)										
	C	O	Al	Si	P	S	Cl	Ca	Fe	Co	Cu
0.25–0.1 mm	48.67	10.19	4.90	0.33	0.17	0.29	2.44	0.24	0.99	20.81	10.96
0.1–0.075 mm	48.80	8.61	2.89	0.90	0.13	–	3.47	0.37	1.21	30.13	3.00
<0.075 mm	50.09	14.59	1.82	0.57	–	–	–	0.38	2.90	29.22	0.42

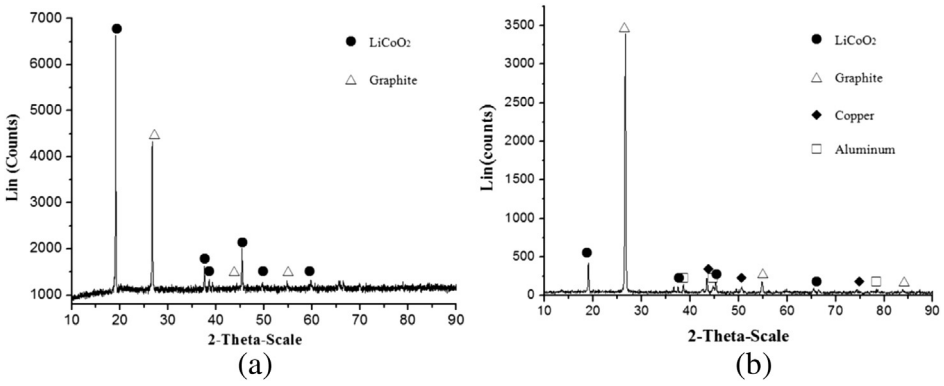

Fig. 9. XRD pattern of 0.25–0.1 mm crushed products: (a) dry crushing, (b) wet crushing.

electrode materials with obvious agglomeration of fine particles because of adhesive.

In dry crushing, all components of LIBs were crushed for a little longer time. Due to the effect of selective crushing, aluminum foil, copper foil, diaphragm and plastic, etc. were not over crushed; in addition, more time was taken for electrode materials such as graphite and $LiCoO_2$ to liberate from copper foil and aluminous foil. And the fine particles, $LiCoO_2$ and graphite in dry crushed products,

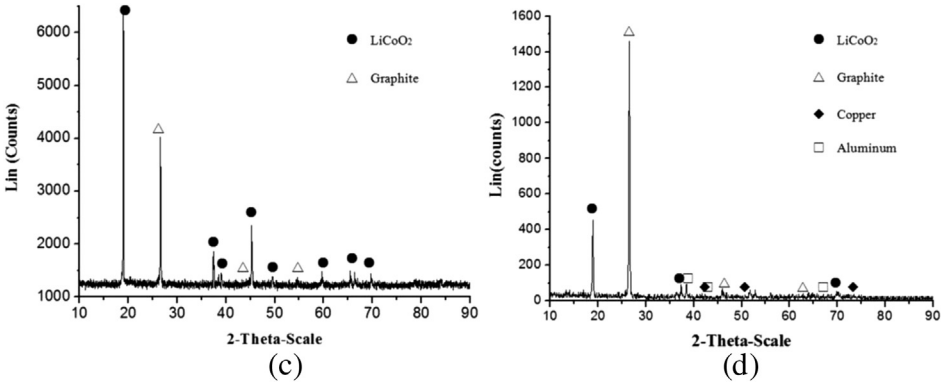

Fig. 10. XRD pattern of 0.1–0.075 mm crushed products: (c) dry crushing, (d) wet crushing.

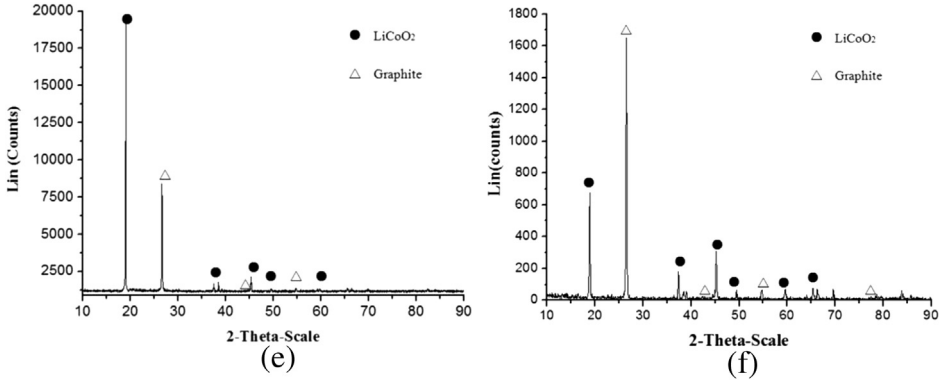

Fig. 11. XRD pattern of −0.075 mm crushed products: (e) dry crushing, (f) wet crushing.

thus, are looser. Although the components in each size fraction of dry crushed products are similar to that of the wet crushing, the content of copper foil, aluminum foil and diaphragm become very few with the decrease of particle size.

Spectra pattern was performed by using EDX. The element content in fine particles of the crushed products with dry and wet method is shown in Tables 1 and 2. Fine materials in the crushed products of spent LIBs mainly contain Co, O and C with trace amount of F, P, Cu, Mn. Because of the water flow introduced in the wet crushing, chemical reactions and hydrolysis of electrolyte $LiPF_6$ and other substances cause the loss of F, P, Mn and bring in impurity element such as Ca, Si, Cl. Wherein Co, Al, Cu and C, as the main components of the electrode material, their levels in the products are the key factors for the assessment of crushing and recovery efficiencies. For dry crushed products, the content of Co was higher, while the level of C, Al, Cu was lower than those of the wet crushing. That is because during the wet crushing process, with the scouring action of the water, the copper foil and aluminum foil enrich to fine particles and meanwhile cause the loss of Co, Mn and other ingredients. Dry crushing takes full advantage of the difference of crushing mechanical properties among each component of spent LIBs and makes selective crushing sticking out. So the component integrity of products can be ensured, also impurities can be avoided.

3.3. X-ray diffraction analysis

So as to further clarify components in −0.25 mm crushed products, X-ray diffraction (XRD) was conducted to characterize the phase composition of −0.25 + 0.125 mm, −0.125 + 0.075 mm and −0.075 mm three crushed products. The results were shown in Figs. 9–11. In the dry crushed products, only $LiCoO_2$ and graphite were detected. While, in wet crushed products, Al and Cu were also detected besides $LiCoO_2$ and graphite. With the decrease of particle size, the fine crushed products under 0.075 mm were almost entirely composed of graphite and $LiCoO_2$. It is further illustrated that because of water scouring in the wet crushing process, besides electrode materials, some other components of spent LIBs enter into the fine fraction and that will not happen in dry crushing process. So, purer electrode materials could be obtained by dry crushing and screening.

4. Conclusions

Mechanical crushing of spent LIBs was studied in detail by comparing the effects of wet and dry crushing methods for the first time. Selective crushing was obviously presented in both wet and dry crushing of spent LIBs. Diaphragm, aluminum foil, copper foil and plastic, etc., mainly existed in coarse particle, while the fine particles were mainly composed of electrode materials such as graphite and $LiCoO_2$. And the dry method can bring selective crushing into full play. Electrode materials such as $LiCoO_2$ and graphite fully shed from aluminum foil and copper foil, then concentrate in fine fraction with less impurities and in loose structure, which created a favorable condition to subsequent recycling. So, the dry crushing method is considered as an advantageous way in the crushing of spent LIBs for their subsequent recycling process.

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